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ASSESSMENT OF HEAVY METAL RESIDUES IN WATER, FLESH, GILLS AND LIVER OF *Tilapia guineensis* AND *Clarias gariepinus* FROM ELEYELE RIVER, IBADAN, NIGERIA

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AUTHORS' CONTRIBUTIONS

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ABSTRACT

Industrialization and urbanization have brought about the contamination of river bodies, resulting in fish and other aquatic contamination. This study investigates the concentration of heavy metal residue such as (Pb, Cd, Cr, Ni, Zn, Mn) in water, flesh, gills and liver of *Tilapia guineensis* **(**tilapia fish) and *Clarias gariepinus* (catfish) collected from the Eleyele river. Fifteen (15) water samples and three (3) fish samples of each specie were collected from five (5) different points along the Eleyele river, including: Oluseyi, Agbaje, Dam, Oba-Ido, and the 'Save and Serve' area. Three treated water samples were also collected from the Eleyele Water Corporation to serve as a control. The residue concentrations of heavy metals in the samples were analysed using Atomic Absorption Spectrophotometer (AAS). The concentrations of Pb ranged from $0.12 \pm 0.02\ to\ 1.13 \pm 0.06 mgL^{-1}$, Cd ranged from $0.09 \pm 0.06\ to\ 0.35 \pm 0.01 mgL^{-1}$, Ni ranged from $0.04 \pm 0.05\ to\ 0.24 \pm 0.07 mgL^{-1}$, Cr ranged from $0.06 \pm 0.07\ to\ 0.12 \pm 0.11 mgL^{-1}$, Mn ranged from 0.06±0.07 to 1.08±0.14. Significant differences in metal concentrations were identified across the various water sampling stations (p0.05) using analysis of variance. The highest (Pb) and least (Cr) values of metal residue concentrations obtained in the two fish species were 2.91±0.11 $mgkg^{-1}$ and 1.07±0.13 $mgkg^{-1}$ respectively. The results of metal concentrations in the gills and liver of catfish were in order of $Pb > Cd > Zn > Cr$, while those of tilapia gills and liver were in the order of $Pb > Cd > Zn > Cr >$ and $Pb > Cd > Zn > Cr$ respectively. The results of water samples, fish flesh and tissues exceeded the recommended values of standard organizations used as references. The minor differences in the results could be attributed to factors influencing metal uptake, such as age, feeding habits, geographic distributions, and species-specific factors. As a result, consumption of aquatic animals can cause acute and chronic diseases in humans and the animals that consume them.

Keywords: Heavy metal; water; tilapia; catfish; fish; flesh; gill; liver.

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1. INTRODUCTION

Heavy metals are defined as metallic chemical that have a relatively high density and are toxic or poisonous at low concentration [1,2]. Pollution of heavy metals in aquatic ecosystem is growing at an alarming rate and has become an important worldwide problem.

Heavy metal contamination of aquatic environments is of critical concern because of their toxicity and accumulation in aquatic organisms. Many dissolved metals entering rivers are adsorbed onto colloid particulates; at high alkalinity and pH, the metals particularly lead and cadmium, precipitate by forming complexes, further influencing the metal toxicity. Aquatic organisms such as phytoplankton, zooplankton, fishes and other higher organisms, during feeding may incorporate these heavy metals into their bodies where they may remain for a very long time in sea foods. Fish is an important source of protein and it also provides essential omega-3 fatty acids (docosahexaenoic and eicosapentaenoic acids) that help to maintain cardiovascular health by playing a major role in the regulation of blood clotting and vessel constriction [3].

The common metals found in fish include potassium, copper, calcium iron, zinc, manganese, mercury, lead, cobalt, chromiun, nickel, arsenic and cadmium [4]. Potassium, phosphorus, calcium, iron, copper, zinc and manganese are essential, while, mercury, lead, cadmium, chromium, and arsenic are non-essential metals of particular concern to surface water system.

Industrial and agricultural activities were reported to be the leading potential sources of the accumulation of pollutants in the aquatic environment including fish consequently, transfers them to human being may accumulate large amount of various heavy metals from the water. Therefore, it is important to determine the concentration of heavy metals in commercial fish and water in order to evaluate the possible risk might contact through fish consumption [5].

The study of micro-nutrients present in living organisms is of biological importance because many of such micro-nutrient take part in some metabolic process and are known to be indispensable to all living things. Fish contain small amount of these micro-nutrient, some of which are essential nutrients, being components that contribute to the growth of the fish. The most important micro-nutrient in form of mineral salts includes calcium, potassium, phosphorus, iron, chlorine, while many others are needed in trace amounts. The deficiencies of these principal nutritional mineral elements induces a lot of malfunctioning, it reduces productivity and causes diseases such as inability of blood clothing, osteoporosis, anemia, etc. The deficiencies of these micro-nutrients, vitamins and protein result in the death of 60% of children under age of 5 years annually in Africa [6]. Furthermore, one major pollution source that pose serious health risk and environmental concern is heavy metals commonly found in fish and aquatic environment. However, aquatic organisms require these minerals elements at moderate levels, but when they exceed metabolic demand or requirement they accumulate in tissues of organisms such as fish. Fish can only metabolize heavy metals to a lesser extent because most of them are non-biodegradable.

Heavy metal comprises a number of elements which are necessary for living organisms, e.g. iron, zinc, copper, magnesium, chromium etc. but these metals are also most important source of pollution.

Heavy metals that accumulate in soils and sediments after weathering process can be deposited in water bodies during surface run-offs, and once they come into the aquatic environment, the heavy metals scatter among the various compounds (water, sediment and biota). Trace metals are in extremely small quantities, and they reside in animals and plant tissues through natural and also artificial (anthropogenic) processes such as agricultural (from fertilizers, weedicides, pesticides etc.) and industrial activities (gaseous and solid wastes). Pollution of aquatic ecosystem has been on the ascendency worldwide [7]. This has been attributed to rapid population growth giving rise to increased urbanization with its attendant increased in agricultural activities and industrialization [8]. Artificially, a variety of pollutants can affect the quality of most natural and manmade water bodies, which receive agricultural, industrial and domestic waste effluents [9].

1.1 Bioaccumulation of Heavy Metals in Fish

The rate of bioaccumulation of heavy metals in aquatic organic depends on the ability of the organism to digest the heavy metals and concentration of such heavy metals in the ecosystem [9]. The distribution of heavy metals in fish species might be as a result of their differences in many factors such as; feeding habit, ecological needs, metabolism, biology and physiology.

Fish can absorb metals dissolved in water and can therefore, provide a reliable indicative of metals in an aquatic ecosystem. Metallic iron transport across the membrane, the metabolic rate of the animal and physio-chemistry of the water and the seasonal changes in the taxonomic status of different tropic levels can significantly affect the toxicity of heavy metals in the fish body [10].

1.2 Pathway of Heavy Metal in Fish

Heavy metals can be incorporated into food chains and absorb by aquatic organisms to a level that might affects their physiological state, the effective pollutant are the heavy metals which have drastic environmental impact on all organisms. Trace metals such as Zn, Cu and Fe play a biochemical role in the life processes of all aquatic plants and animals; therefore they are essential in the aquatic environment of fish. Fishes are most important organisms in the aquatic food chain, which are sensitive to heavy metals contaminant. This energy stored by plant is passed along the ecosystem in series of feeding system (food chain). Food chain is known of energy transfer and nutrient from organisms to organisms in feeding pathway.

1.3 Effect of Heavy Metals in Fish

The normal respiratory activity of the fish was also affected significantly along with significant decline in the hematological parameters, total glycogen, lipids and protein contents of the fish. The gills of tilapia exposed to aluminum alone showed a severe fusion of lamellae and filaments and started secretion of large amount of mucus while structural lesions were reduced by the addition of Ca^{2+}or Na^{+} in the water along with Al. In an aquatic environment, waterborne heavy metals are easily taken up by the aquatic organisms and start accumulation in the tissue. Fish accumulate toxic chemicals such as heavy metals directly from water and diet, and contaminant residue may ultimately reach concentrations hundreds or thousands of times above those measured in the water, sediments and food.

2. MATERIALS AND METHODS

2.1 Materials

The materials used for this research were dissecting tray, dissecting instrument, petri-dish, cardboard, hand sanitizer, disposable hand gloves, hand towel, tape rule, paper tape, permanent marker, analytical weighing balance, beaker, erlenmeyer flask, measuring cylinder, volumetric flask, fume cupboard, Atomic Absorption Spectrophotometer (AAS).

2.2 Description of the Study Area

The Eleyele River is situated upstream on the river Odo-Ona in the city of Ibadan within Geographical Coordinates: Latitude 7°20' N – 7°25' N and Longitude 3°51' E – 3°6' E. It falls within the Ido Local Government area of Oyo state, Nigeria and the lake has a length of 240 m across the dam, a catchment area of 323.7 sq km, and an impoundment area of 156.2 hectares with a storage capacity of 29.5 million litres of water. Eleyele Water Works is located at the close end of works road which is accessed through Eleyele roundabout on Sango Eleyele Road, just downstream of the confluence of river Odo-Ona and river Alapata. The Odo-Ona river, on which the dam is built, traverses many locations within Ibadan metropolis and goes as far as Apata and Omi-Adio. Beyond that margin of woodland, there is urban development on all sides of the reservoir. Eleyele reservoir is located to the North-West of the Ibadan city center bounded by Eleyele urbanization in the South, the area of Apete in the East, Awotan in the North, and Ologuneru in the North-West.

2.3 Samples Collection

Three (3) adult tilapia and catfish were procured from fishermen at the band of the Eleyele river and put in an ice pack to retain the freshness of the fishes and transported (less than an hour) to the laboratory, weighed, and total length recorded.

Three (3) water samples were collected each from five (5) different points along the Eleyele river at Oluseyi, Agbaje, Dam and Oba-Ido. Water Works was where the control was collected. One litre of each water sample was collected in a plastic bag, pre-soaked in 1 mole of trioxonitrate (V) acid (nitric acid) overnight, rinsed with tap water and finally with deionised water, after which they were rinsed two times with the sample to be collected.

2.4 Sample Preparation And chemical Analysis

The fish samples were rinsed with distilled water and the scales of Tilapia fish were removed. The fish were dissected to remove the gills, liver and flesh using stainless steel instruments and digested.

1 g of the samples was digested with nitric acid and perchloric acid in a ratio (1:1) followed by sulphuric acid, and the mixture was heated until a clear solution was attained. The complete digest was cooled to room temperature. Finally, the digest was filtered using whatman 42 filter paper and made up to a 100 mL scale with distilled water. The digestion of each sample was made in triplicate and analyzed for Pd, Cd, Zn, Cr and Mn using Atomic Absorption Spectrophotometer (AAS BK$-$320N) after selecting the appropriate wavelength at which each heavy metal

was determined. Three analytical blanks were performed to test for possible contamination. The results obtained were expressed in mgL^{-1} for the water sample and $mgkg^{-1}$ for flesh, gills and liver.

2.5 Quality Control and Assurance

Quality control was assured by the analysis of reagent blanks and procedural blanks, and also, samples were analyzed in triplicates.

All the reagents used for the analysis were of analytical grade and pre-tested for possible heavy metal contamination. The instrument used was calibrated and standardized with standard solutions prepared from commercially available chemicals. Distilled water was used throughout the study. The glasswares and containers used to collect water samples were soaked in 10 % nitric acid for 24 hours before being rinsed with distilled water, then 0.5 % (w/v) potassium permanganate $(KMNO_4)$ solution and finally with distilled water.

2.6 Statistical Analysis

Analyses of samples were carried out in triplicates. Statistical analysis of data was carried out by using the Statistical Package for Social Science (SPSS) version 15.0. The means of replicates and evaluation of significant differences between different samples were determined using descriptive statistics and analysis of variance (ANOVA) respectively. One way analysis of variables (ANOVA) was used to test for a significant difference in the concentrations of heavy metals in the flesh, gills and liver of the fish samples and water collected from the various sites of the river.

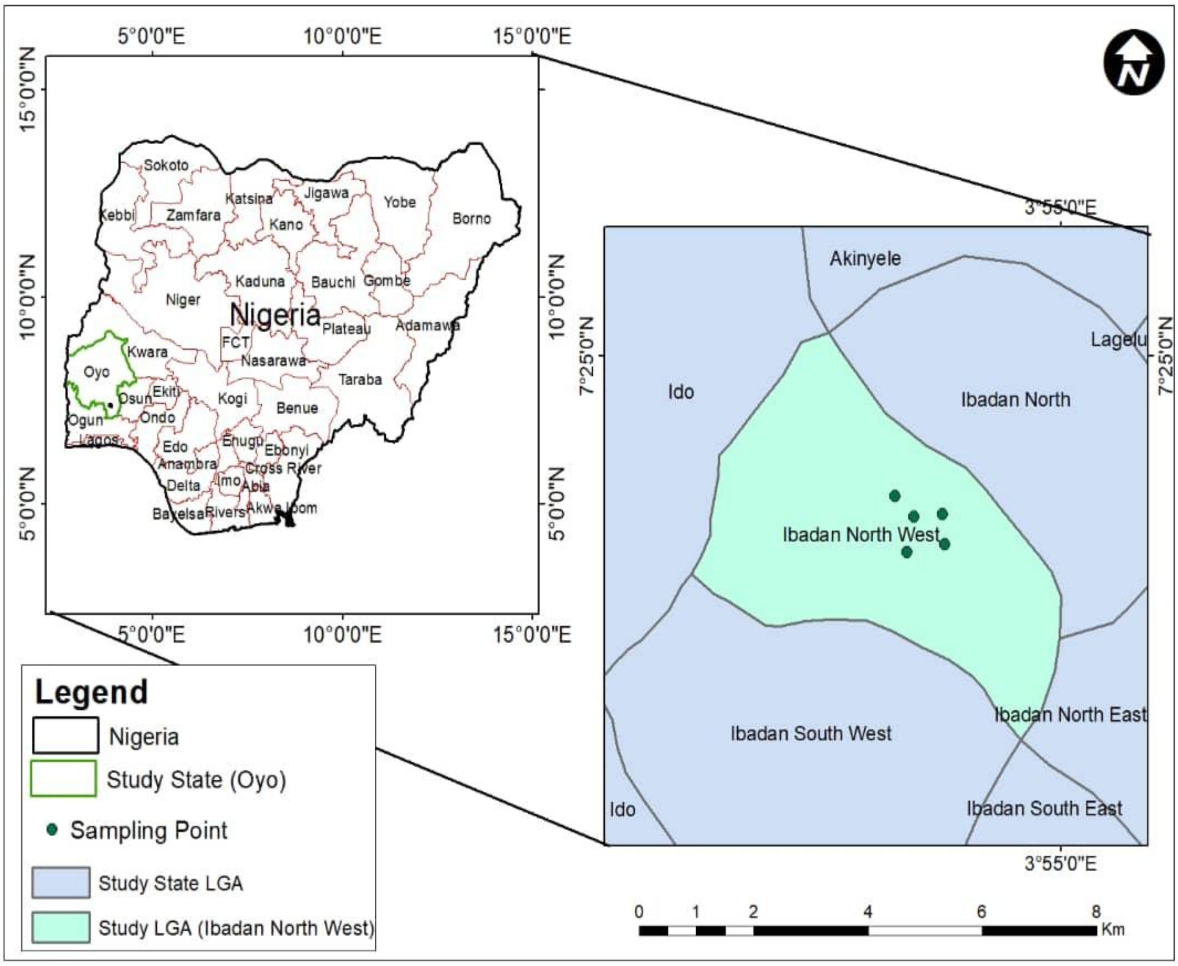

Fig. 1. Map of the study area

3. RESULTS AND DISCUSSION

3.1 Heavy Metal Residues in Water Samples of Different Points from Eleyele River

Table 1 shows the results of heavy metal analysis of water samples collected at different points around the Eleyele River. The mean lead concentration varied from $0.04 - 1.63 mgL^{-1}$. The highest value was found at the Agbaje sampling point, while the lowest was found at the control sampling point. Cadmium concentration varied from $0.01 - 0.35\ mgL^{-1}$ with the highest value found at the Agbaje sampling point and the lowest at the control point. Chromium concentration varied from $0.02 mgL^{-}$ to $0.01\ mgL^{-1}$, the highest value was obtained at both the Agbaje and Oluseyi sampling point, while the least value was obtained at Dam, 'Save and serve' and Oba-Ido. Nickel and cobalt were not detected in the water samples. Analysis of variance shows that a significant difference exists in the mean metal concentrations detected across the various sampling points (p<0.05).

The concentration of heavy metal residues in the water samples varies due to different collection points. The Pd contents of all water samples are higher than the permissible limits of WHO [11] and SON [13]. The concentrations of Cd in the water samples are also higher than WHO and SON. The result of Cr content in all water samples are higher than the recommended values of WHO [11], FEPA [12] and SON [13]. The contents of and Mn in all water samples collected are greater than the recommended permissible limits of the reference standard.

The highest concentration of heavy metals was observed at Agbaje point (Pb 1.13±0.06 mgL^{-1} and Mn 1.08±0.14 mgL^{-1}), while the least of metals parameters analysed in all the water samples was obtained in the control. (Pb 0.12±0.02 mgL^{-1} and 0.04±0.05 mgL^{-1}). The higher metal concentration in the river at the Agbaje sampling point might be due to the illegal dumping of solid waste refuse into the river at this spot.

3.2 Heavy Metal Residues in Fish Flesh, Gills and Liver of Tilapia and Cat Fish from Eleyele River

The mean concentrations of heavy metals in the flesh and gills of the two species of fish samples are shown in Table 2. The Pb concentration in the flesh of the two fish species ranged from $2.91 \pm 1.02\ mgkg^{-1}$ to $2.91 \pm 1.11\ mgkg^{-1}$. The concentrations of Cd in tilapia flesh were higher than catfish and ranged from $1.36 \pm 0.12 mgkg^{-1}$ to $2.54 \pm 0.08 mgkg^{-1}$. The concentrations of Cd in the gills and liver of the two fishes ranged between 3.04±0.17 $mgkg^{-1}$ to 3.38±0.06 $mgkg^{-1}$. The concentration$,Cr$ and Zn ranged from 1.07±0.13 $mgkg^{-1}$ to 1.87±0.09 $mgkg^{-1}$. The concentration in the tilapia liver shows the highest content (3.42±0.09 $mgkg^{-1}$) while the concentrations of Cr in catfish flesh recorded at the least (1.07±0.13 $mgkg^{-1}$). The results of this study do not show any significant differences ($p > 0.05$) in both flesh and tissues analysed.

Fishes are at the top of the aquatic food chain and accumulate large amounts of heavy metals from water and sediments. The heavy metal content in the two species of fish is not significantly different from each other (p>0.05). Although, the values of metal content obtained in the flesh and tissues of the fish species were higher than the recommended permissible limit of FEPA [12], except for catfish flesh, which was lower than the recommended value. This observation has been widely reported in other studies in fish [14,15]. Other aquatic animals like crabs have also been reported to have higher levels of heavy metals than some recommended standards [16]. Other heavy metals such as nickel, chromium and cobalt were not detected in the fish flesh and gill samples. Therefore, a regular monitoring of the river for toxic pollutants is very important.

Table 1. Heavy Metal Residues (mgL^{-1}) in water samples from different points of the Eleyele River

Sampling Point	Pb	Cd	Ni	Cr	Mn
Agbaje	1.13±0.06^{a}	0.35±0.01^{a}	0.24±0.07^{a}	0.12±0.11^{a}	1.08±0.14^{a}
Oluseyi	0.58±0.06^{bc}	0.26±0.04^{ab}	0.19±0.03^{b}	0.16±0.09^{a}	0.67±0.08^{b}
Dam	0.87±0.03^{b}	0.17±0.03^{b}	0.29±0.05^{a}	0.14±0.06^{b}	1.03±0.05^{a}
Save and Serve	0.74±0.04^{b}	0.25±0.01^{ab}	0.25±0.03^{a}	0.18±0.12^{a}	0.59±0.12^{b}
Oba- Ido	0.46±0.01^{c}	0.19±0.04^{b}	0.17±0.01^{b}	0.14±0.03^{b}	0.71±0.05^{b}
Control	0.12±0.02^{d}	0.09±0.06^{c}	0.04±0.05^{c}	0.06±0.07^{c}	0.06±0.07^{c}
WHO [11]	0.05	0.003	0.005	0.05	0.02
FEPA [12]	<1.00	<1.00	<1.O0	<1.00	0.05
SON [13]	0.01	0.03	0.02	0.05	0.50

Means with the same subscript are not significantly different (p > 0.05)

Table 2. Heavy Metal Residues ($mgkg^{-1}$) in the Flesh, Gills, and Liver of Tilapia and Catfish from Eleyele River

Sample part	Pb	Cd	Ni	Cr	Zn
Tilapia Flesh	2.91 ± 0.11^{b}	$2.54 \pm 0.08^{\mathbf{b}}$	2.27 ± 0.13^{b}	2.41 ± 0.21^{a}	1.87 ± 0.09^{c}
Tilapia Gills	$3.52 \pm 0.95^{\mathbf{a}}$	$3.16 \pm 0.1.4^{\mathbf{a}}$	2.34 ± 0.16^{b}	2.47 ± 0.09^{a}	2.61 ± 0.06^{a}
Tilapia Liver	4.12 ± 0.86^{a}	3.38 ± 0.06^{a}	3.42 ± 0.09^{a}	2.58 ± 0.06^{a}	2.87 ± 0.15^{a}
Catfish Flesh	$1.46 \pm 1.02^{\mathbf{c}}$	1.36 ± 0.12^{c}	1.19 ± 0.29^{c}	1.07 ± 0.13^{c}	1.26 ± 0.04
Catfish Gills	$3.32 \pm 1.48^{\mathbf{b}}$	3.04 ± 0.17^{a}	2.08 ± 0.08^{bc}	1.96 ± 0.13^{b}	2.07 ± 0.18^{b}
Catfish Liver	3.94 ± 0.81^{a}	3.25 ± 0.06^{a}	2.52 ± 0.14^{b}	2.35 ± 0.07^{a}	2.46 ± 0.13^{a}
Eleyele River	1.18±0.94	0.01±0.02	ND		ND
WHO [11]	2.00	2.00	0.6	0.15	−
FAO [17]	0.50-6.00	0.05-5.50	−	1.00	−
FEPA [12]	2.00	−	0.50	0.15	−

Means with same subscript are not significantly different ($p > 0.05$)

4. CONCLUSION

The study was conducted to investigate the concentration of heavy metals Pb, Cd, Ni, Cr and Zn in the flesh, gills and liver of tilapia and catfish and also the quality of the water collected at different points of the Eleyele river. The results of $Pd, Cd, Ni,$ Cr and Mn in water samples collected from different points of the Eleyele river are above all recommended standards of permissible limits used as reference in this study, except in the controls that are below the recommended value of SON [13]. The values of metals detected in the flesh and tissues of the two fish species are above the recommended permissible limits of WHO [11] and FEPA [12].

Difference in heavy metals bioaccumulation between the two fish species might be due to different in feeding habits, diets, pollution exposure, age size, weight, length and ecological behavior, among others. This study revealed that gills and liver accumulated more heavy metal residues than flesh.

It can be concluded that adequate precaution measures need to be taken to ensure monitoring of the water quality of Eleleye River. This can be achieved through appropriate regulatory measures on hazardous waste containing heavy metals and by discouraging the discharge of untreated industrial sewage. Legislative law should be enacted to protect and improve the quality and resources of this river in order to prevent future contamination of fish and human domestic uses of the water. Furthermore, more research centers should be established to aid in more frequent and thorough checks of these metals in the environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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